Heats of Mixing of Dichloroethane with Non-polar Liquids

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In a number of papers[1] concerning the solutions of non-electrolytes published hitherto, the discussions were made from the standpoint of inter-molecular energy. However, in solutions containing steric isomers due to the internal rotation[2], their intra-molecular energy may be expected to contribute to the thermodynamical effects of solutions and this fact has not been discussed before.

In the following section of this report, we shall derive a simple theory about the excessive enthalpy arising from the internal rotation and compare it with experimental data of the heats of mixing of dichloroethane with cyclohexane, carbon tetrachloride and benzene, where dichloroethane is the typical molecule having isomers owing to the internal rotation.

Solutions of Dichloroethane with Non-polar Solvent.—It is well known that molecules of dichloroethane can exist in the *trans* and the *gauche* form. In the gaseous state, the potential energy of the former is lower than that of the latter by about 1.5 kcal./mole and the molecules of dichloroethane exist predominantly in the *trans* form at room temperature.

In the liquid state, however, the *gauche* form with a large dipole moment is considerably more stabilized than the *trans* one by the reaction field from the surrounding dielectric medium, so that a considerable part of the molecules is in the *gauche* form. When a non-polar solvent of a lower dielectric constant is added to the pure liquid of dichloroethane,

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[1] A. Münster, *Trans. Faraday Soc.*, **46**, 165 (1950); J. S. Rowlison, ibid., **50**, 1036 (1954); J. Barker, *J. Chem. Phys.*, **20**, 794 (1952); H. Tompa, ibid., **21**, 250 (1953); J. A. Pople, *Discussions Faraday Soc.*, **15**, 35 (1953); etc.

[2] S. Mizushima, "Structure of Molecules and Internal Rotation". Academic Press Inc., Publishers. New York, N. Y. (1954).

the dielectric constant of the surrounding medium of the dichloroethane molecules become lower, resulting in transition from the *gauche* form to the *trans*. Owing to this transition, the change in ethalpy which does not appear in ordinary solutions will be expected to occur in these solutions.

We suppose that the solution contains N_d molecules of dichloroethane and N_s molecules of solvent. Of N_d molecules of dichloroethane, N_t molecules are in the *trans* form and N_g in the *gauche*, that is, $N_d=N_t+N_g$.

We further make the following assumptions;

1) Internal partition functions of dichloroethane in the *trans* and in the *gauche* form are the same.

2) A part of inter-molecular energy, arising from dispersion force between both forms and solvent molecules are the same.

3) The part of inter-molecular energy arising from the dipole of the dichloroethane molecule in the *gauche* form are included in the mutual energy between the dipole and the reaction field.

4) The sizes of the dichloroethane and the solvent molecules are nearly equal.

5) On the mixing of the solution, no volume change occurs, that is, the volume of the solution is additive.

Under these assumptions the configurational partition function Z of the solution is represented by the following equation;

$$Z=2^{N_g}\phi_d{}^{N_t+N_g}\phi_s{}^{N_s}\frac{(N_t+N_g+N_s)!}{N_t!\ N_g!\ N_s!}\times e^{-Xw/RT}e^{-N_g(\Delta E-\Delta G)/kT} \tag{1}$$

where ϕ_d and ϕ_s are the internal partition functions of the dichloroethane and the solvent molecule, X the number of pairs of the dichloroethane-solvent and $2w$ defined as follows:

$2w=2w_{ds}-w_{dd}-w_{ss}$, where w_{ds}, w_{dd} and w_{ss} are the ordinary interaction energy of dichloroethane-solvent pair, dichloroethane-dichloroethane pair and solvent-solvent pair, respectively. ΔE is the internal potential energy difference between the *trans* and the *gauche* form. ΔG is the stabilization free energy of a dipole arising from the reaction field of surrounding dielectric medium.

Assuming the simplest model in which the dichloroethane molecule is spherical and the dipole is at the center of this sphere, ΔG can be represented as follows3);

$$\Delta G=(1/2)\mu^2{}_gR/(1-R\alpha_d),$$
$$R=2(\varepsilon-1)/(2\varepsilon+1)a^3{}_d \tag{2}$$

where μ_g is the dipole moment of the *gauche* form, a_d is the molecular radius of the dichloroethane molecule assumed to be spherical, α_d is the polarizability of dichloroethane and ε is the dielectric constant of the solution.

Naturally, ε in the formula (2) is dependent on N_g and N_s, and is expressed by the following formula4);

$$\begin{aligned}\varepsilon-1=\frac{3\varepsilon}{2\varepsilon+1}\Bigg\{&\frac{4\pi\mu^2{}_gN_g}{3kT}\left(\frac{2\varepsilon+1}{2\varepsilon+n^2{}_d}\cdot\frac{n^2{}_d+2}{3}\right)^2\\&+\frac{2\varepsilon+1}{2\varepsilon+n^2{}_d}(n^2{}_d-1)\times\frac{4\pi}{3}a^3{}_dN_d\\&+\frac{2\varepsilon+1}{2\varepsilon+n^2{}_s}(n^2{}_s-1)\times\frac{4\pi}{3}a^3{}_sN_s\Bigg\}\end{aligned} \tag{3}$$

where n_d and n_s are the refractive indices of dichloroethane and solvent respectively and a_s is the molecular radius of solvent molecule assumed to be spherical.

To obtain the ratio of N_g to N_t, we shall assume that the chemical potential of the *trans* form is equal to that of the *gauche*, that is,

$$\partial\ln Z/\partial N_g=\partial\ln Z/\partial N_t$$

and then we can derive

$$\begin{aligned}N_g/N_t=2\exp-\{&\Delta E\\&-(\Delta G+N_g\partial\Delta G/\partial N_g)\}/kT\end{aligned} \tag{4}$$

Using (4), we now proceed to obtain the excess enthalpy of the solution. Enthalpy of the solution arising only from the internal rotation is expressed as follows;

$$H_i=kT^2(\partial\ln Z/\partial T)-Xw \tag{5}$$

The excess of enthalpy is obtained by subtracting the value of H_{i0} of pure liquid of dichloroethane from the above. Thus the excess of enthalpy is

$$\Delta H_i=H_i-H_{io} \tag{6}$$

where H_{io} is the enthalpy of dichloroethane in the pure lipuid state.

We shall apply this treatment to the actual systems. In the measurement of heats of mixing, cyclohexane, carbon tetrachloride and benzene were used as non-polar solvents, but here in the calculation we shall take up only the dichloroethane-carbon tetrachloride system. Other two systems may be expected to show only a small deviation from the carbon tetrachloride system, because the refractive indices of benzene and cyclohexane are

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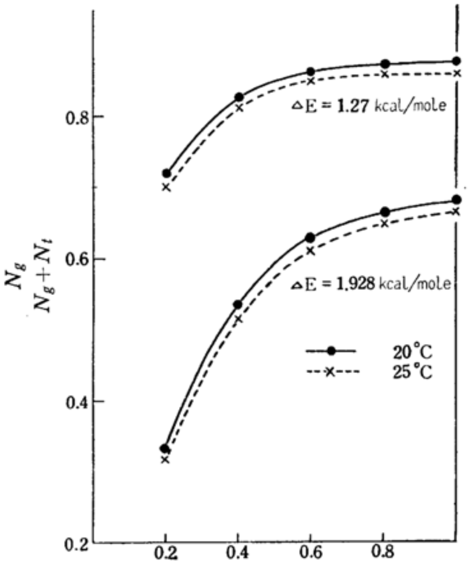
3) C. G. Böttcher, "Theory of Electric Polarization," Elsevier, Houston, p. 139.

4) H. Fröhlich, "Theory of Dielectrics", Oxford, London, p. 47.

little different from that of carbon tetrachloride. The values of refractive index n and molar volume of dichloroethane and carbon tetrachloride in the pure liquid used in the calculations are as follows;

	n^2		Molar volume (ml.)	
	20°C	25°C	20°C	25°C
Dichloroethane	2.0861	2.0702	79.03	79.88
Carbon tetrachloride	2.1316	2.1220	96.49	97.08

According to Wada and Morino[5], we adopt $\Delta E = 1.27$ kcal/mole and $\mu_g = 2.55$ D. To obtain the values of N_g/N_t, we have to perform successive approximations using formula (4). The results thus obtained are plotted against the concentration of dichloroethane in Fig. 1. It is seen that the fraction of the *gauche* form decreases appreciably with dilution of dichloroethane by carbon tetrachloride. There have been no reports on systematic experimental data to be compared with the above expectation. Only in the pure liquid of dichloroethane**, it was found from spectroscopic data that the fraction of the *gauche* form is about 2/3, and is somewhat lower than the calculated value. This may be attributed, as Wada[6] pointed out, to the calculation on the oversimplified spherical model of molecule and may be improved by various corrections.



Mole Fraction of Dichloroethane

Fig. 1

To diminish the overestimation of the energy due to the reaction field, it will be necessary to increase the value of ΔE. We, therefore, adopted a larger value of 1.928 kcal./mole as ΔE, with which the value 2/3 of the fraction of the *gauche* form in pure liquid was obtained. By the use of this value as ΔE, the fraction of the *gauche* form is recalculated and shown in the same figure. Here, it will also be seen that the appreciable decreases in the fraction of the *gauche* form take place with dilution by carbon tetrachloride. Hence we may use both values of ΔE in the later calculation.

Knowing the values of $N_g/(N_g+N_t)$ and using Eqs. (5) and (6), we can calculate the values of the excess of enthalpies of the solution. As in the formula (5), $N_g/(N_g+N_t)$, ε and n are all dependent on temperature, the explicit derivation of (5) is complicated. Consequently the following formula may be used instead of (5).

$$H_i = -k\{(\ln Z_1 - \ln Z_2)/(1/T_1 - 1/T_2)\} - xw$$

where Z_1 and Z_2 are the partition functions at the different temperatures T_1 and T_2, and here as T_1 and T_2 the values of 298.16 and 293.16°K will be used respectively.

The excess of enthalpies of the solution calculated is shown in Fig. 2. From this figure it will be seen that a fairly large amount of heat, in particular when the value of $\Delta E = 1.27$ kcal./mole is used, is to be absorbed when dichloroethane and carbon tetrachloride are mixed.

Experimental

In order to compare these theoretical results with the experiment, we measured the heat of mixing of dichloroethane with cyclohexane, carbon tetrachloride and benzene at 25°C.

These four materials were purified according to the method described in the literature and finally distilled by a long column of about thirty theoretical plates and the fractions having the boiling point range of 0.1°C were taken. The apparatus used for the measurement was already described elsewhere[7] and in this experiment it was improved in some points. The temperature sensitivity of the apparatus was 1.5×10^{-5}°C, which corresponds to the heat sensitivity of 10^{-3} cal.

Results and Discussion

The results obtained for the three systems are shown in Tables I, II and III, respectively. Heats of mixing per mole

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[5] A. Wada and Y. Morino, *J. Chem. Phys.*, **22**, 1276 (1954).

** Private communication from Mr. I. Miyagawa.

[6] A. Wada, *J. Chem. Phys.*, **22**, 198 (1954).

[7] K. Amaya and R. Fujishiro, This Bulletin, **29**, 270 (1956).

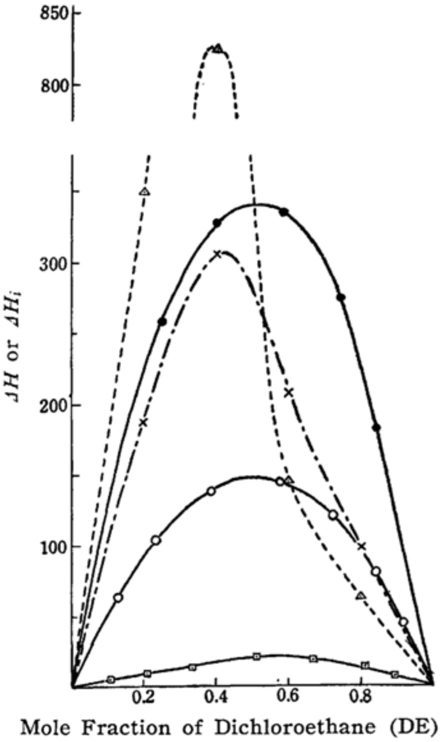

Fig. 2.

Expt.
—●— *DE*-cyclohexane
—○— *DE*-carbon tetrachloride
—▣— *DE*-benzene
Calcd.
---△--- ΔE=1.27 kcal./mole
-·-×-·- ΔE=1.928 kcal./mole

TABLE I

HEAT OF MIXING FOR DICHLOROETHANE-CYCLOHEXANE SYSTEM (25°C)

Mole fraction of dichloroethane	ΔH/mole of sol. cal.
0.2551	260.9
0.4065	326.5
0.5781	330.8
0.5781	329.8
0.7326	271.8
0.8457	186.0

TABLE II

HEAT OF MIXING FOR DICHLOROETHANE-CARBON TETRACHLORIDE SYSTEM

Mole fraction of dichloroethane	ΔH/mole of sol. cal.
0.1284	64.2
0.2324	104.1
0.3992	141.6
0.5695	146.8
0.5535	155.6
0.7219	124.8
0.8423	81.8
0.9139	48.0

TABLE III

HEAT OF MIXING FOR DICHLOROETHANE-BENZENE SYSTEM

Mole fraction of dichloroethane	ΔH/mole of sol. cal.
0.1114	6.66
0.2026	11.5
0.3340	17.6
0.5084	22.6
0.5138	19.1
0.6740	20.2
0.8043	16.6
0.8938	10.9

of mixtures are plotted in Fig. 2, in which the theoretical curves are also shown.

Since the observed heats of mixing contain not only the contribution from the dipolar energy but also that from the dispersion energy, we have to estimate the part of the contribution from the latter and derive that from the former to compare it with the theory. A molecule of *trans*-dichloroethylene is nearly isoelectric with that of dichloroethane and has a dipole moment of zero; it seems to be reasonable to assume that the contribution of the dispersion energy is nearly the same for both molecules.

So we took the molecule of dichloroethylene as an imaginary molecule of dichloroethane with zero dipole moment and estimated the part of the contribution from dispersion forces for dichloroethane, using the data for *trans*-dichloroethylene. Expected heat of mixing of dichloroethylene with three solvents was calculated for equimolar mixture of dichloroethylene and three solvents according to the Scatchard formula*** for three equimolar mixtures of dichloroethylene: 23 cal./mole for cyclohexane, 18 cal./mole for carbon tetrachloride and nearly zero for benzene.

These corrections seem to be relatively small for each case, so we did not make any corrections of the observed heats of mixing. Since these non-polar liquids used as solvents have nearly equal values of dielectric constant, it is not unreasonable to expect from the theory that the values of ΔH_i for these systems are nearly equal to one another. However, the observed values of heats of mixing, which may be taken as values of ΔH_i disregarding the minor corrections mentioned above, do not coincide with one another; the maximum values of the heats of mixing per

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*** Joel H. Hildebrand and Robert L. Scott, "The solubility of nonelectrolytes". Reinhold Publishing Co., New York (1948). p. 124.

mole of mixture are 330 cal., 150 cal. and 20 cal., for the systems of cyclohexane-dichloroethane, carbon tetrachloride-dichloroethane and benzene-dichloroethane, respectively.

These discrepancies seem to show that the simple assumption of taking dichloroethylene as an imaginary dichloroethane of zero dipole moment can not be necessarily applied to these systems to estimate the contribution from dispersion forces.

As for the comparison with the theoretical value, the value of ΔH_i obtained by the use of the value of 1.27 kcal./mole for ΔE is much greater than the observed value and this may be due to the overestimation of the reaction field in the simple Onsager model.

By the use of the higher value of 1.928 kcal./mole for ΔE to diminish the overestimation of the reaction field, rather good agreements between the theory and the experiment were obtained for the systems of cyclohexane-dichloroethane and carbon tetrachloride-dichloroethane. But such a higher value of ΔE seems to be inconsistent with the experimental fact, so that these discrepancies may have to be explained by considering two dipoles in the dichloroethane molecule with proper angles between them, as was done by Wada⁶⁾, or by some other more refined theory of dielectrics.

For the benzene-dichloroethane system, the agreement is very poor and the deviation is negative. This will suggest that the specific interactions occur between these two kinds of molecule. More quantitative discussions for these systems will be impossible until more data concerning various physical properties are accumulated.

Summary

For three solutions of dichloroethane which is regarded as a typical molecule having internal rotation isomers, the excessive enthalpies arising from the internal rotation were calculated according to a simple theory derived from the Onsager model, and were compared with the results obtained from the measurements of heats of mixing for these solutions. The agreement was not very good and it seems to owe to the overestimation of the reaction field based on the simple molecular model in the Onsager model. Especially for the dichloroethane-benzene system, special interactions may be expected to exist between dichloroethane and benzene.

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